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Semiconductor Surface Chemistry

A Major Qualifying Project Report

Submitted to the Faculty

of the

WORCESTER POLYTECHNIC INSTITUTE

in partial fulfillment of the requirements for the

Degree of Bachelor of Science

By:

Brian Hamilton _____

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Approved:

Professor Ronald L Grimm, Primary Advisor

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Abstract

Thin layers of stibnite (Sb_2S_3) crystals have been analyzed by Fourier-Transform Infrared Spectroscopy (FT-IR). Following this analysis, the surface of the metal was changed by etching the stibnite with various organic compounds. The resulting surface was analyzed with FT-IR again, and compared against the original spectrum. Additionally, the surface was analyzed by X-Ray Photoelectron Spectroscopy (XPS) in order to verify the quality of the stibnite surface and quantify the degree of surface oxidation.

Acknowledgements

I would like to thank Mr. Andy Butler for his generosity in training me on the proper use of the IR Spectroscope for analysis in my experiments.

I would like to thank Professors Sal Triolo and Drew Brodeur for their assistance in utilizing the IR software in Goddard Hall.

Above all, I would like to thank Professor Ronald Grimm for his assistance and mentorship during this project, and for sharing his knowledge with me throughout the year.

1.Introduction

As we as a society continue to deplete our reserves of fossil fuels, we must also continue to develop an alternative form of energy to replace fossil fuels that is both sustainable and practical. Solar energy is one of these potential sources for renewable, efficient energy. This project researches one possible alternative semiconductor source for future solar panels.

Stibnite, Sb_2S_3 , has a band gap of $1.7 \text{ eV}^{[1]}$, which means that an electron must have that much energy in order to jump from the valence band to the conduction band. A band gap of this size, from a solar energy perspective, would be able to conduct more amperage than the silicon that is currently used in solar panels, whose band gap is $1.1 \text{ eV}^{[2]}$.

As in a typical solar panel cell, sunlight would hit the cell and excite the electrons in the stibnite, sending them into the conduction gap. Wiring would then correct the electronic imbalance, which conducts usable electricity, after it is converted from DC to AC ^[3].

By utilizing stibnite in solar panels, we would eliminate the need for silicon to be crystallized, both as a mono crystalline or polycrystalline structure, which could make them both cheaper and more efficient.

2. Background

Despite their numerous practical applications, there has been little research devoted to “mid” gap semiconductors. Increasing the available knowledge on these chemical, specifically stibnite, could represent the future of efficient solar energy conversion. This project focuses on gathering a precise IR and XPS (X-ray Photoelectron Spectroscopy) spectrum of stibnite. The stibnite was then functionalized with various organic compounds, and subsequent IR and XPS spectra were taken in order to compare to previous spectra. This comparison would show the changes on the surface, as a result of the functionalization. The structure of stibnite is found below in Figure 1.

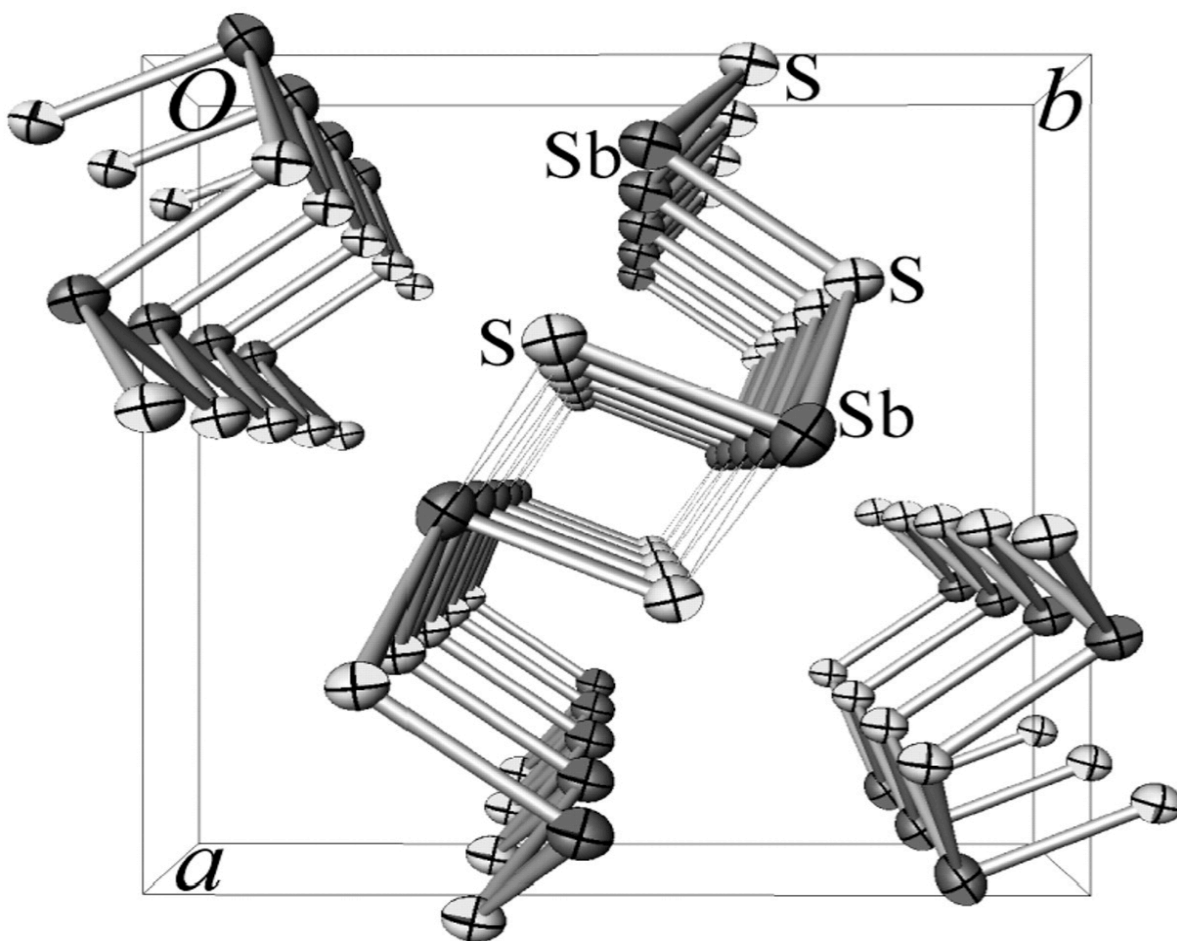


Figure 1: Structure of Stibnite

As shown in the figure, the stibnite is found in layers as a crystal. Because there are no strong interactions between the individual layers, a thin layer of stibnite can easily be removed from the rest of the crystal and used for further surface analysis.

The purpose of functionalization in this experiment is to remove hydrocarbon contamination from the surface, which is important for the use of solar panels because hydrocarbons absorb some light in the ultraviolet range, which would decrease the amount available to participate in solar energy conversion.

2.1 IR Spectroscopy

IR spectroscopy was used to analyze the surface of the stibnite by use of transmission spectra. Transmission spectra analyze the light that passes through the sample in the instrument. Because of the nature of transmission spectra, a thin layer of the stibnite must be used so that light still is able to pass through the sample, in order to be analyzed. Additionally, the sample must be angled at the Brewster angle, so that the refractive index of the stibnite allows for light to pass through the sample.

2.2 X-Ray Photoelectron Spectroscopy

X-Ray photoelectron spectroscopy (XPS) is a quantitative surface spectroscopic technique that analyzes the composition of a material's surface. Operating at an ultra-high vacuum, (typically on the order of 10^{-9} millibar, the level of an Ultrahigh vacuum, or UHV), XPS operates by bouncing high intensity x-rays onto a material's surface, which causes the material to emit photoelectrons. These photoelectrons are then collected and analyzed for the amount that is released at each particular binding energy, measured in eV. Based on the value of the binding energy, and the size of the resulting peaks, it can be definitively determined what resides on the surface of a material. For example, both the Nitrogen 1s electron and the Scandium 2p electron are released at a binding energy of 398.4 eV. However, the Nitrogen will only have one peak and the Scandium will have 2, the other peak being at 401.0 eV, with a height ratio of approximately 3:1, respectively ^[4]. XPS can also be used to determine the empirical formulas of the chemicals on the surface of the sample. This results in an absolute, quantified analysis of the surface of a sample.

Detection is limited to both elements and concentration, however. XPS cannot detect Hydrogen or Helium, but can detect elements with an atomic number of 3 (Lithium) or higher with typical x-ray equipment. Additionally, it cannot detect elements with a concentration below parts per thousand in typical settings. Chemicals with this concentration can be detected if they are concentrated at the surface, or if the instrument collects data on the sample for an extended period of time; however this prolonged exposure to high intensity x-rays will likely begin to degrade the quality of the sample being analyzed, and as such, this method should be used sparingly.

3. Experimental

3.1 IR Spectroscopy

Due to the nature of solids in transmission IR analysis, the stibnite had to be loaded into the machine at its Brewster angle. This was determined by the following formula:

$$\theta_B = \arctan\left(\frac{n_2}{n_1}\right)$$

where θ_B is the Brewster angle, n_1 is the refractive index of the medium, and n_2 is the refractive index of the sample. Using values of 1.0002772 and 2.65 for n_1 and n_2 , respectively, the Brewster angle was determined to be 69.3° [5, 6]. A visual representation of the Brewster angle is shown below.

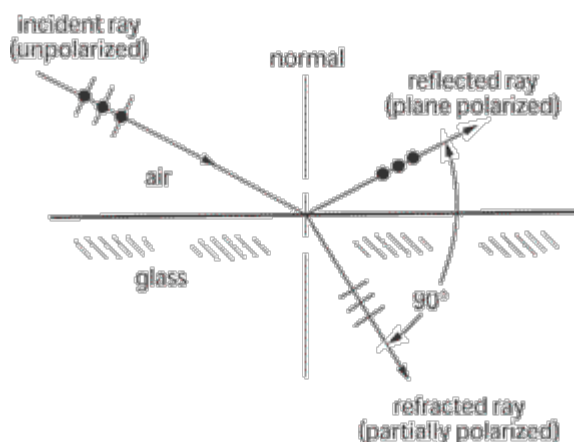


Figure 2: The Brewster angle

The angle from the incident ray to the normal is defined as the Brewster angle, 69.3° in the case of Stibnite.

A sample of stibnite was loaded into a Perkin Elmer Spectrum One FT-IR and placed at the Brewster angle. Rather than take the background as air, the background was chosen to be the sample of stibnite before any surface chemistry had been conducted on it. Once this background was taken, the stibnite was taken out and functionalized by etching the metal for ten seconds in a 10% solution of hydrochloric acid. The sample was then placed back in the instrument and analyzed like a normal sample, yielding negative peaks in the hydrocarbon region. These

negative peaks indicate that the surface of the stibnite had been cleared of hydrocarbon contamination. On a separate piece of stibnite, another IR spectrum was taken, this time, having air as the background and both the before and after etching spectra as regular spectra. Both spectra are shown in Appendix A as Figures 4 and 5.

3.2 Determination of the Proper XPS settings

Due to the novel nature of the XPS instrument, analysis had to be conducted on the proper settings of the instrument and software to find a balance between the resolution of the spectrum, or the number of electrons emitted from the metal by the bombardment of x-rays, and the pass energy of the instrument. Additionally, the time it takes for the data to be collected played a significant role in determining the ideal settings. The ideal settings on the XPS will provide minimal noise on the spectrum, as well as thin peaks at each of the points at which certain electrons are released. Attaining a balance between these will likely occur during one of the middle pass energies, 23.50 to 58.70 eV, as the lower energies tend to have thin peaks, but a lot of noise, and the higher energies tend to have wider peaks without noise. Additionally, the ideal spectrum will have a high count for the number of electrons emitted, something else at which, the higher pass energies excel.

3.3 XPS Spectroscopy

A sample of stibnite was loaded into a PHI 5600 XPS system and analyzed using the following procedures.

3.3.1 Loading the Sample

Samples are loaded into the XPS using the following specifications. First, the “Backfill Intro” button on the Automatic Valve Control (AVC) was pressed in an effort to equalize the pressure inside the chamber with outside pressure. Once pressure regulates, open the hatch and place the sample on the sample puck in the arm. The cover to the hatch is then replaced and the “Pump Into” button on the AVC is hit. The various vacuum attached to the Intro Chamber will get the pressure as low as possible, before introducing them to the main analysis chamber. This process takes approximately 30 minutes to complete. Once the intro chamber is prepared, the “Intro Sample” button is pushed. Quickly after, push the arm is slowly pushed out, currently containing the sample into the main analysis portion of the instrument. At this point, internal pressure will spike, rising to as high as 10^{-6} , but this is purely a result of the vacuums in the intro

chamber not being strong enough to relieve as much pressure as the more specialized vacuum in the main chamber.

Once the arm is fully extended, the z-axis controller must be raised so that the puck sits on the holder. The x and y-axis controllers may have to be changed in order to completely catch the puck. Upon securing the puck on the holder, the arm is slowly pulled back, and the valve between the intro chamber and main chamber closes at a certain point.

3.3.2 Obtaining X-rays for the Device and Conducting a Spectrum

Once the sample is loaded into the XPS, the decision must be made if analysis will be done on the twin anode or mono anode. Furthermore, if the mono-anode is chosen, another decision must be made between the large and small anode. Simultaneously, the power to the analysis instruments, control box, and analysis software must be turned on in that order. Grimm group uses AugerScan for their XPS analysis software. Upon turning the x-rays on, the filament is selected, based on the anode chosen earlier. After ensuring that all knobs read 0, voltage is slowly brought up to 10 kV, and power is slowly brought up to 300 W, while keeping the voltage at 10 kV. Subsequently, both voltage and power are brought to the target values, as determined by the experimental conditions.

To collect a spectrum, a new survey or multiplex must be created. A survey will take the entire span of the binding energies, from 1400, for the aluminum filament, to 0 eV; whereas a multiplex will allow you to only analyze that are immediately adjacent to the peaks, but will be able to collect more relevant data in a shorter time.

As a safety precaution, ensure that the pressure of the main chamber is at most in the range of 10^{-8} millibar before starting the x-rays to ensure safety.

3.3.3 Removing sample

In order to remove the sample that is not currently in a UHV, the “pump intro button must be hit on the AVC and it must decrease the internal pressure for at least half an hour. After waiting the elapsed time, or if the sample begins in a UHV, the x, y, and z-axes must be lined up to collect the puck, and the “Intro Sample” button on the AVC must be hit. Upon this, the arm is slowly pushed into the chamber until it connects with the puck. The z-axis is then dropped so that the puck will not hit the holder when it is being drawn back into the Intro Chamber. After

slowly pulling the arm back, a valve will close and isolate the Intro Chamber, allowing it to be backfilled by pressing “Backfill Intro” in the AVC. Once the pressure is relieved, the sample can be removed from the XPS instrument.

3.4 Etching the Samples

After the initial spectrum was taken on each metal sample, they were etched with a 10% hydrochloric acid solution to remove all hydrocarbon contamination from the surface. Each sample was taken out of the instrument, dropped in the hydrochloric acid solution for 10 seconds, and taken out to be analyzed again by the same methods

4. Results & Discussion

4.1 IR Results & Discussion

The negative peaks in my absorbance spectrum indicate that the surface was changed from the baseline. This is to be expected, and even is the desired outcome, because there was no hydrocarbon peak around 3000 cm^{-1} , indicating that there are no hydrocarbons present on the surface of the metal sample.

This is also shown in the spectra comparing the pre and post etched samples of stibnite against the background of air. Though the peaks are very similar, the lack of a hydrocarbon peak shows that the experiment was successful in regards to removing the contamination from the surface. A closer look at the spectra is shown in Figure 3 below:

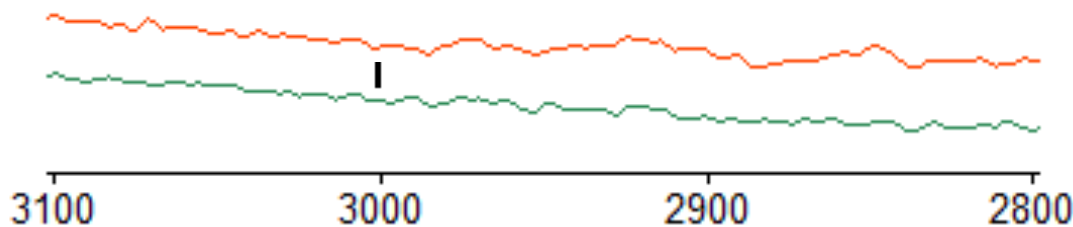


Figure 3: Closer Look of IR spectra Before (Orange) and After (Green) etching. The Black Bar Represents 4×10^{-4} Absorbance

As shown above, the differences between the etched and non-etched samples are indicative of a lack of hydrocarbons on the surface. As seen in the spectra, there is a distinct gap between the absorbance level of the etched and the non-etched version of stibnite in this spectrum. This is likely due to differences in positioning the metal sample in the beam of the FT-IR, rather than a chemical change as a result of the etching. The absorbance scale was removed in this figure in order to ease the visual comparison and a bar scale was added.

4.2 XPS Results & Discussion

Due to a technical malfunction with the instrument, I was unable to conduct the XPS portion of my experiment. If the instrument had work properly, however, I expect that the XPS spectrum would have look similar to the spectrum I took prior to conducting the pass energy

analysis and was more focused on learning how to properly conduct and interpret these novel spectra. However, the peaks would all be smoother, as this spectrum was at a lower pass energy. This spectrum is found in Figure 6 in Appendix B.

The large peaks at around 530 eV are indicative of antimony, as the 3d electron give peak readings of 528.2eV and 537.6 eV. Also for antimony, the 3p electrons are emitted at 766.4 and 812.6, both of which are found in the spectrum. The large peak at 1030 eV is suggestive of antimony's Auger electron. For the sulfur, the small peaks around the area of 163.9 and 165.1 are indicative of its presence in the sample. The distinctive peak at 285 eV is certainly that of carbon's 1s electron ^[4]. This carbon could be a result of hydrocarbon contamination or an impurity remaining from the adhesive used to secure the stibnite to the analysis puck.

After etching the stibnite, I expect that the small peak at 285 eV would have disappeared, as the hydrocarbons would no longer be present on the surface of the metal. In order to quantify the degree of surface oxidation, I would also expect small oxygen peaks in the range of 530-533 eV and very small chlorine peaks around 198.8 eV ^[4].

4.3 Full Width at Half Maximum

The full width at half maximum is a function that would describe the width of a spectroscopic peak at half of its maximum height. This would yield a good interpretation of how compact the spectrum is, especially since these spectra do not have sharply defined edges. The XPS spectra will be more accurately able to be defined using this method. A smaller value for the full width at half maximum (FWHM) is of course desired, but with the lower pass energies, there is typically too much noise in the spectrum to have an accurate measurement of FWHM. Figures 8-17 in Appendix B show the spectra of each available pass energy.

This data was collected on a sample of stibnite from 545 to 520 eV, which is the area of the Sb 3d electron is released. Table 1 below shows the relationship between each of the available pass energies and its respective electron count at 400 W, 14 kV, and utilizing the mono-large setting.

Pass Energy (eV)	Max Count	eV/step	# Sweeps	FWHM (eV)
2.95	32	0.025	10	3.3
5.85	444	0.025	10	1.55
11.75	1336	0.025	10	1.6
23.50	3136	0.025	10	2.125
29.35	4120	0.125	50	2.25
46.95	6897	0.200	80	2.4
58.70	8942	0.125	20	2.375
93.90	13870	0.200	80	2.8
117.40	16843	0.125	50	2.875
187.85	23619	0.0200	80	3.4

Table 1: Analysis of counts using 400 W, 14 kV, and mono-large

Though the count increased with increasing pass energy, the pass energy of 29.35 eV was determined to have the best balance between resolution and time taken to collect the sample. The resulting XPS spectrum is shown in Appendix B. Additionally, the XPS spectrum of this particular pass energy provides the best balance between FWHM and noise.

5. Conclusions

Though an XPS spectrum was not able to be taken, the IR analysis of the stibnite surface will be sufficient analysis was able to conclude that the hydrocarbon contamination was removed from the surface of the stibnite. Based on the results found in the experiments and research conducted, I believe that stibnite could be either a suitable replacement for silicon in solar panels, or paired with silicon and be equally efficient.

6. References

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6. "Optical Constants of AirCiddor 1996 - N 0.23-1.690 μm ." *Refractive Index of Air*. Web.

Appendix A: IR Spectra

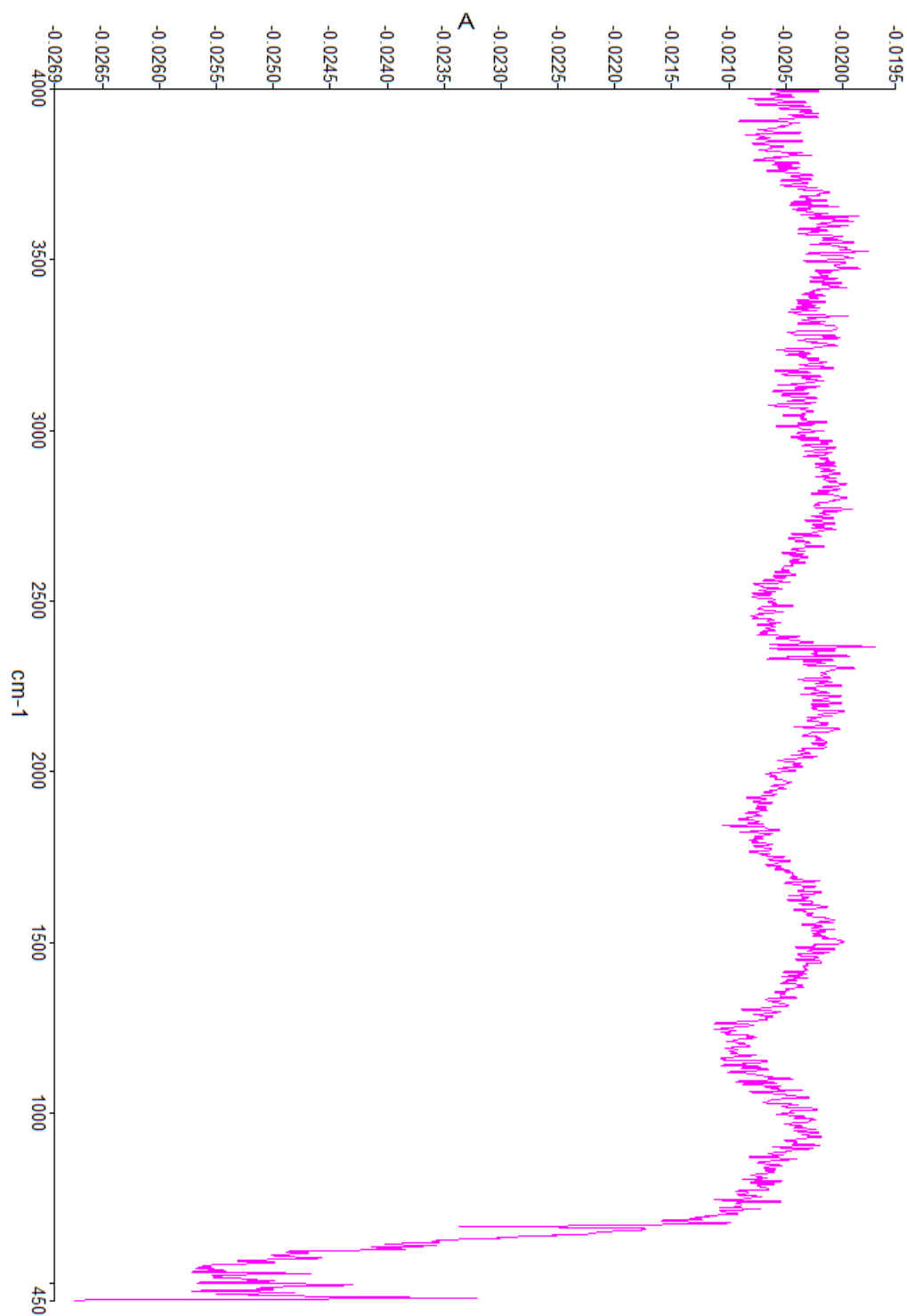
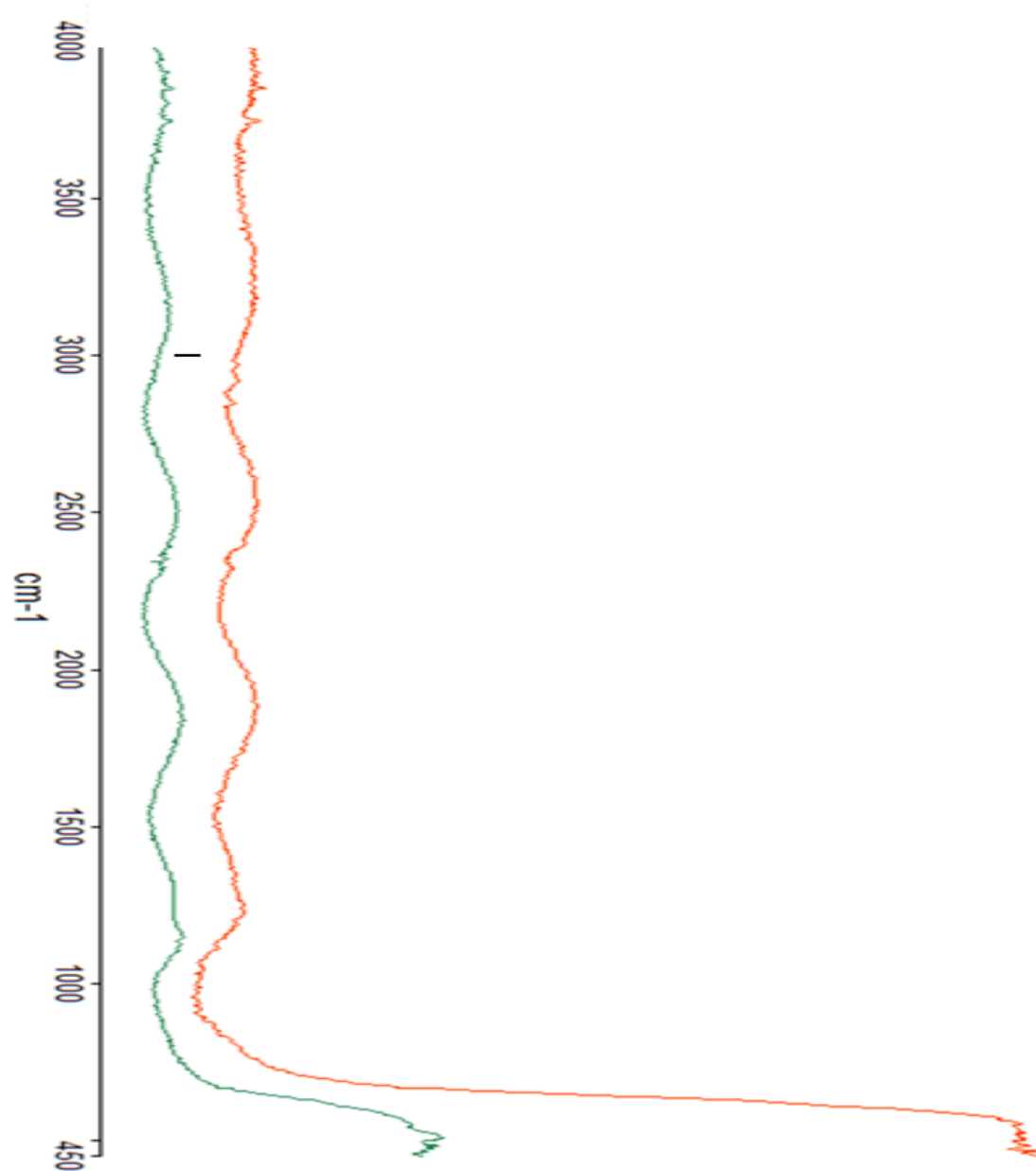


Figure 4: Absorbance Spectrum of Etched Stibnite Using Unetched Stibnite as the Background



Appendix B: XPS Spectra

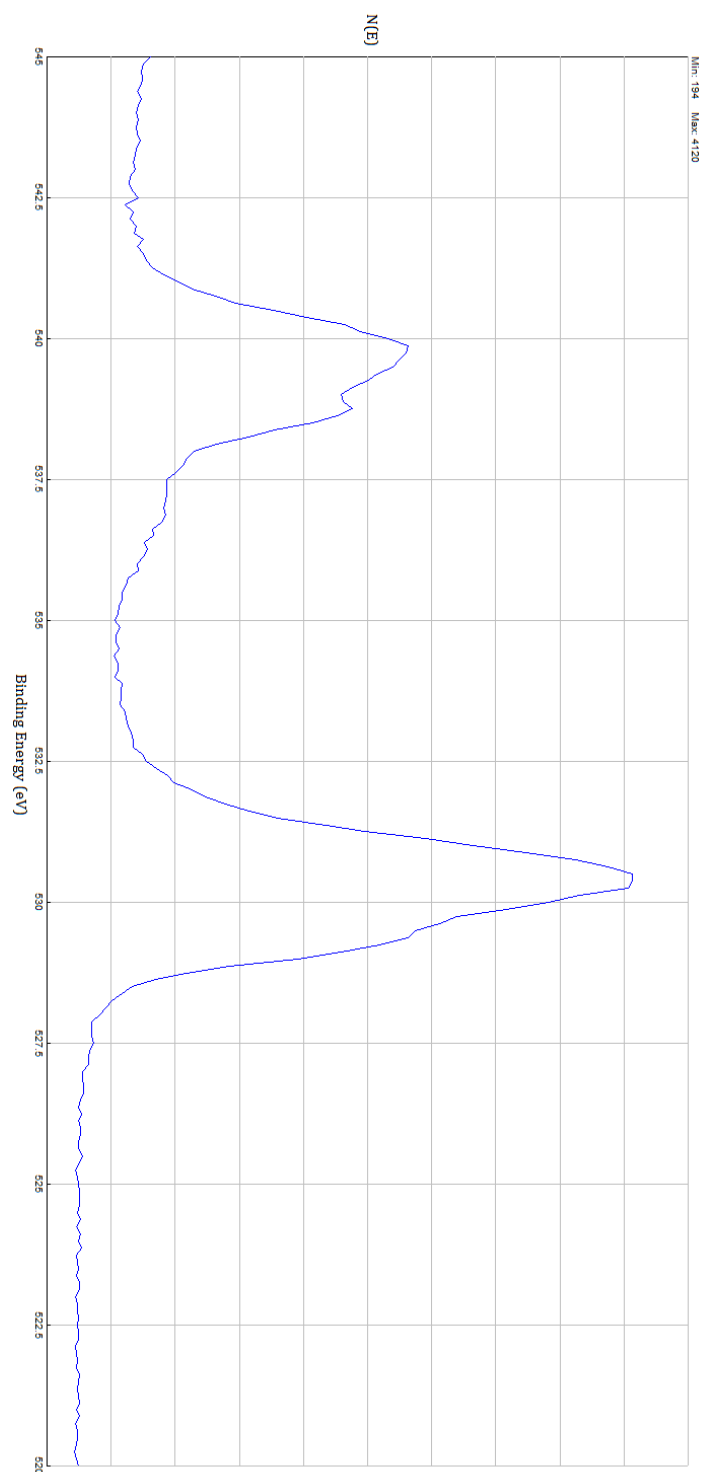


Figure 6: XPS Spectrum of Stibnite from 545 to 520 eV, run at 0.125 eV/step, 50 msec/step, and at a pass energy of 29.35

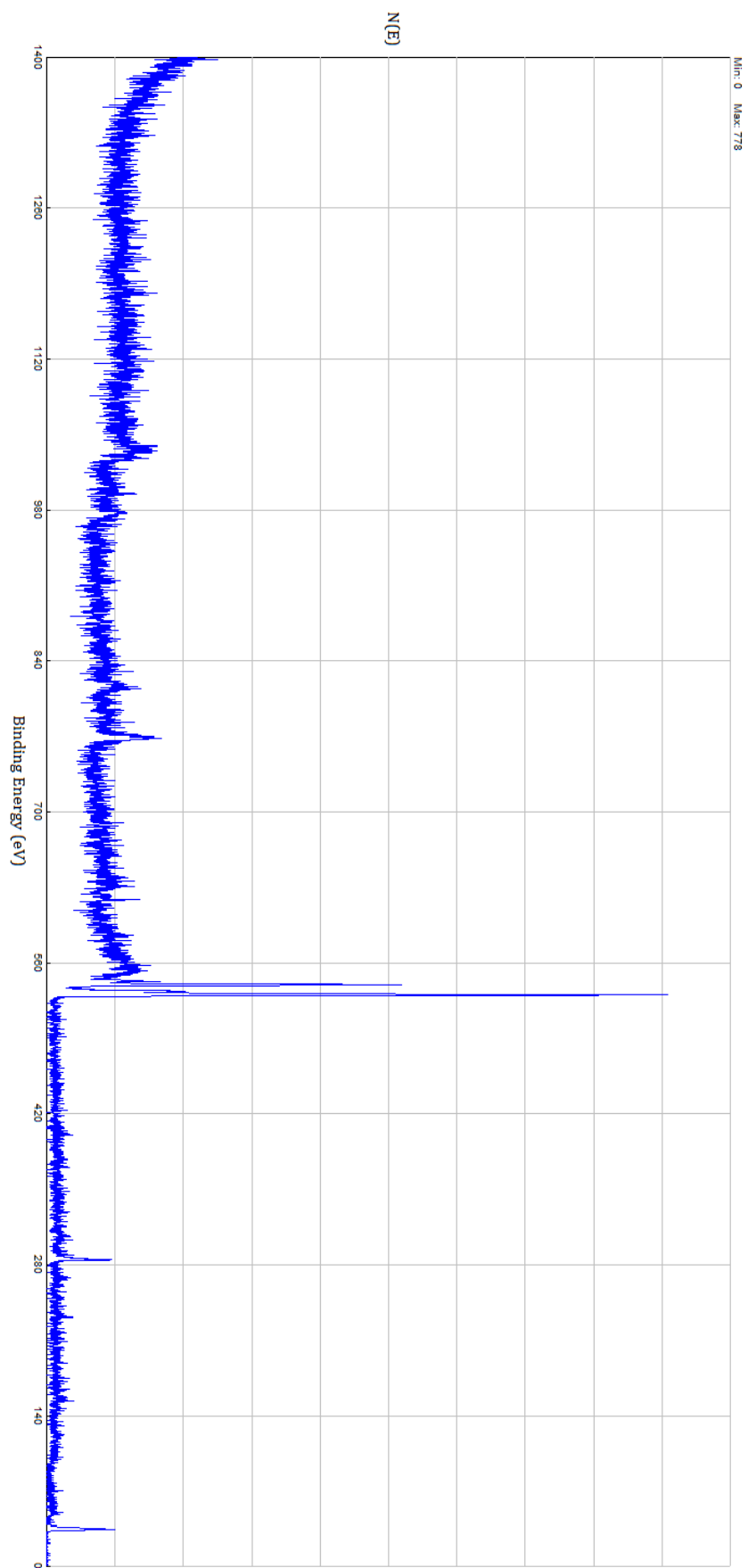


Figure 7: XPS Spectrum of Stibnite

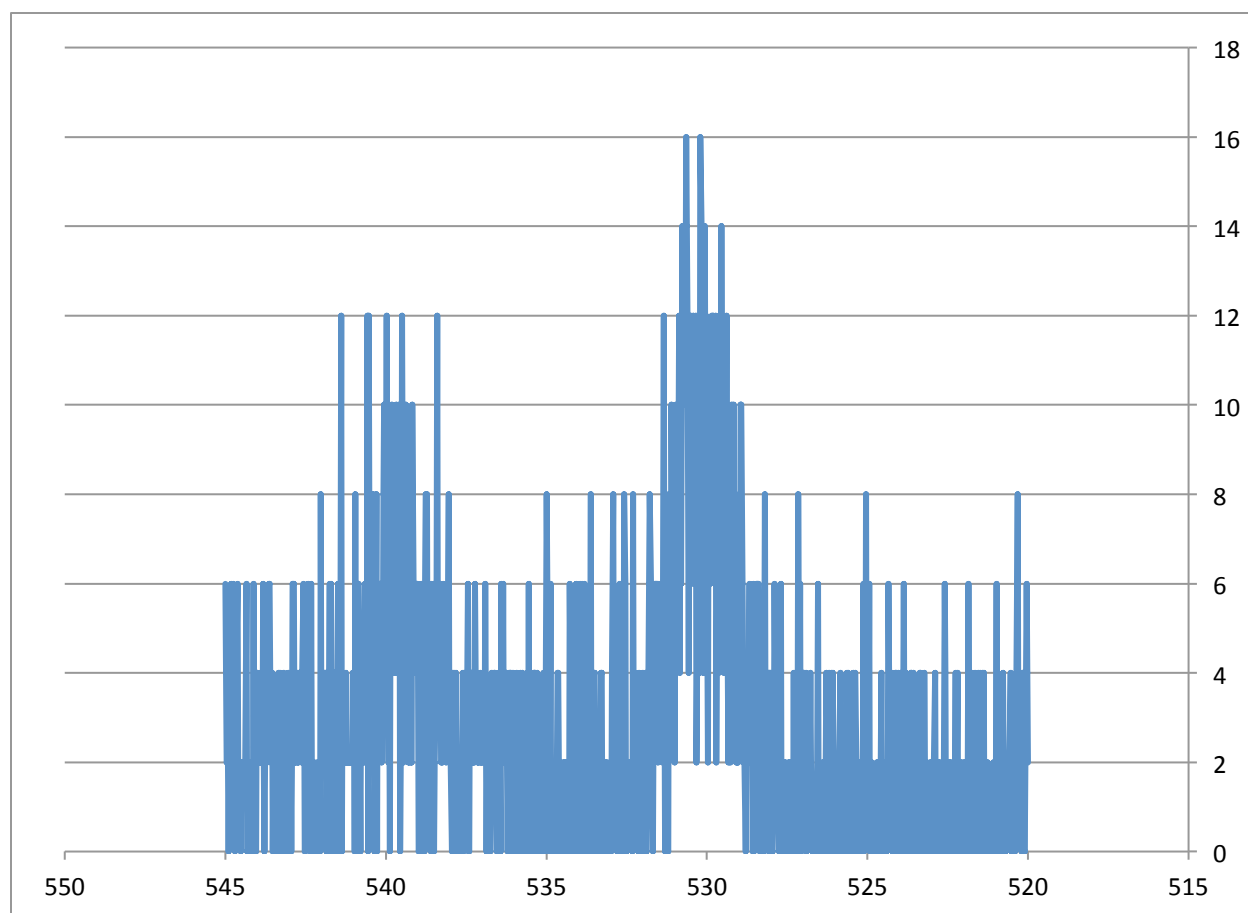


Figure 8: XPS Spectrum of the Sb 3d region (545 - 520 eV) at a Pass Energy of 2.95 eV

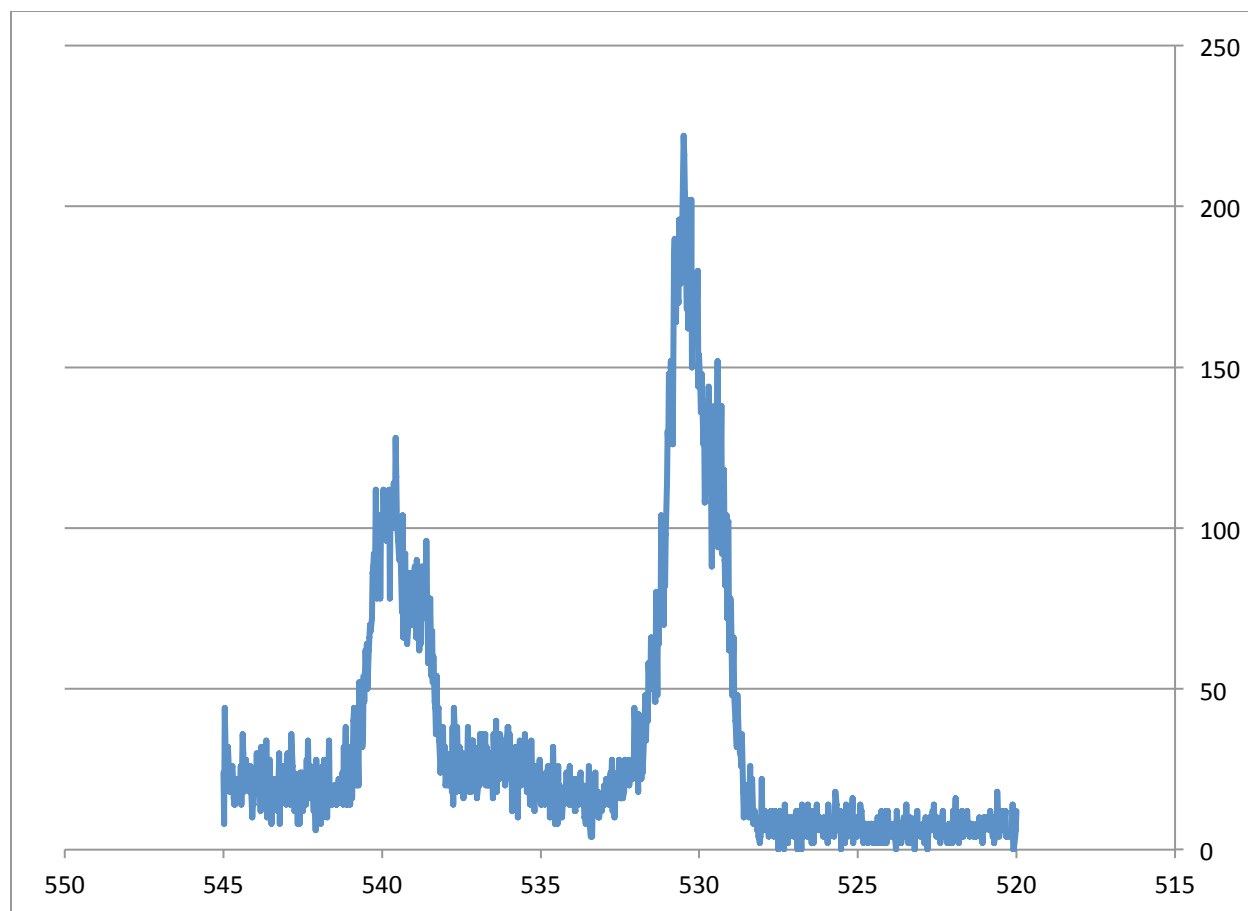


Figure 9: XPS Spectrum of the Sb 3d region (545 - 520 eV) at a Pass Energy of 5.85 eV

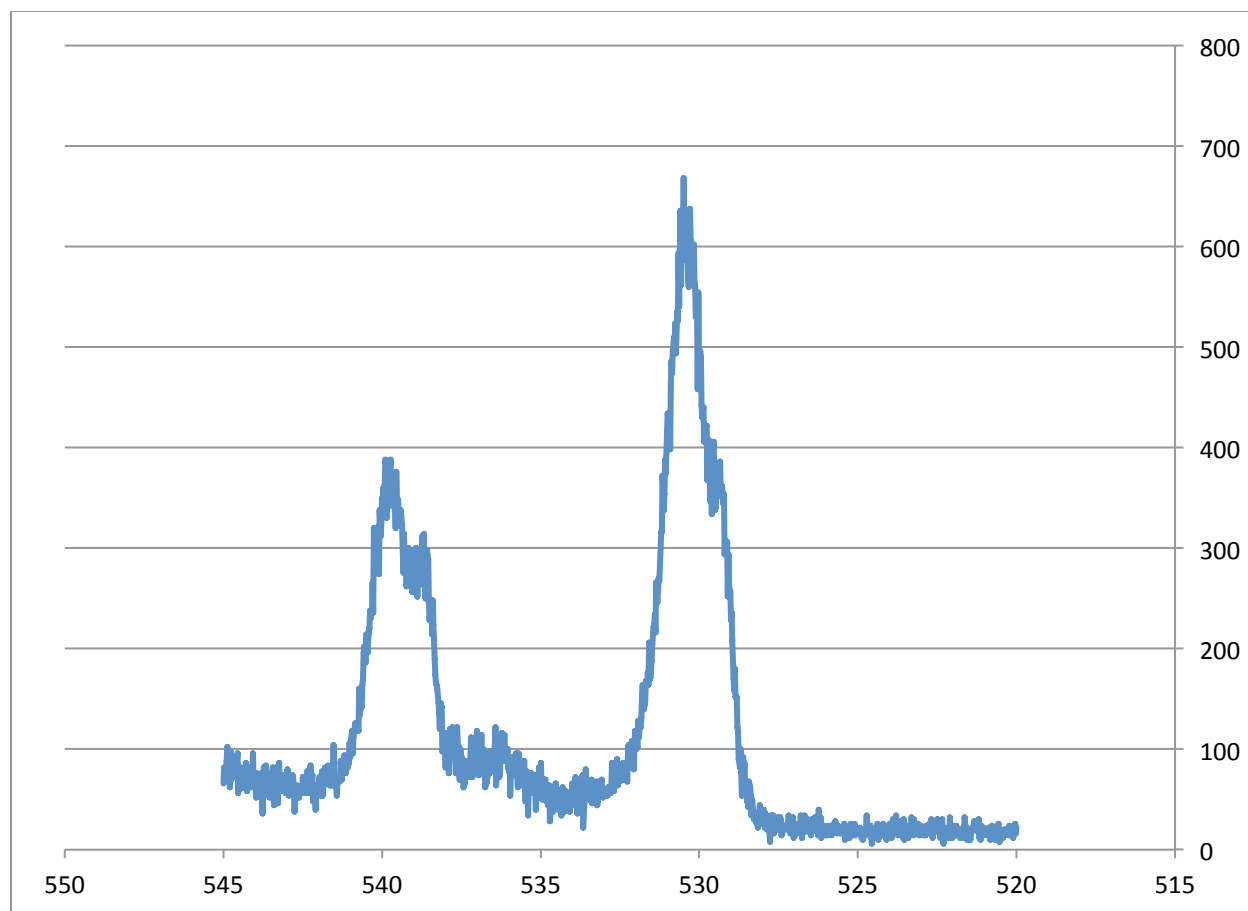


Figure 10: XPS Spectrum of the Sb 3d region (545 - 520 eV) at a Pass Energy of 11.75 eV

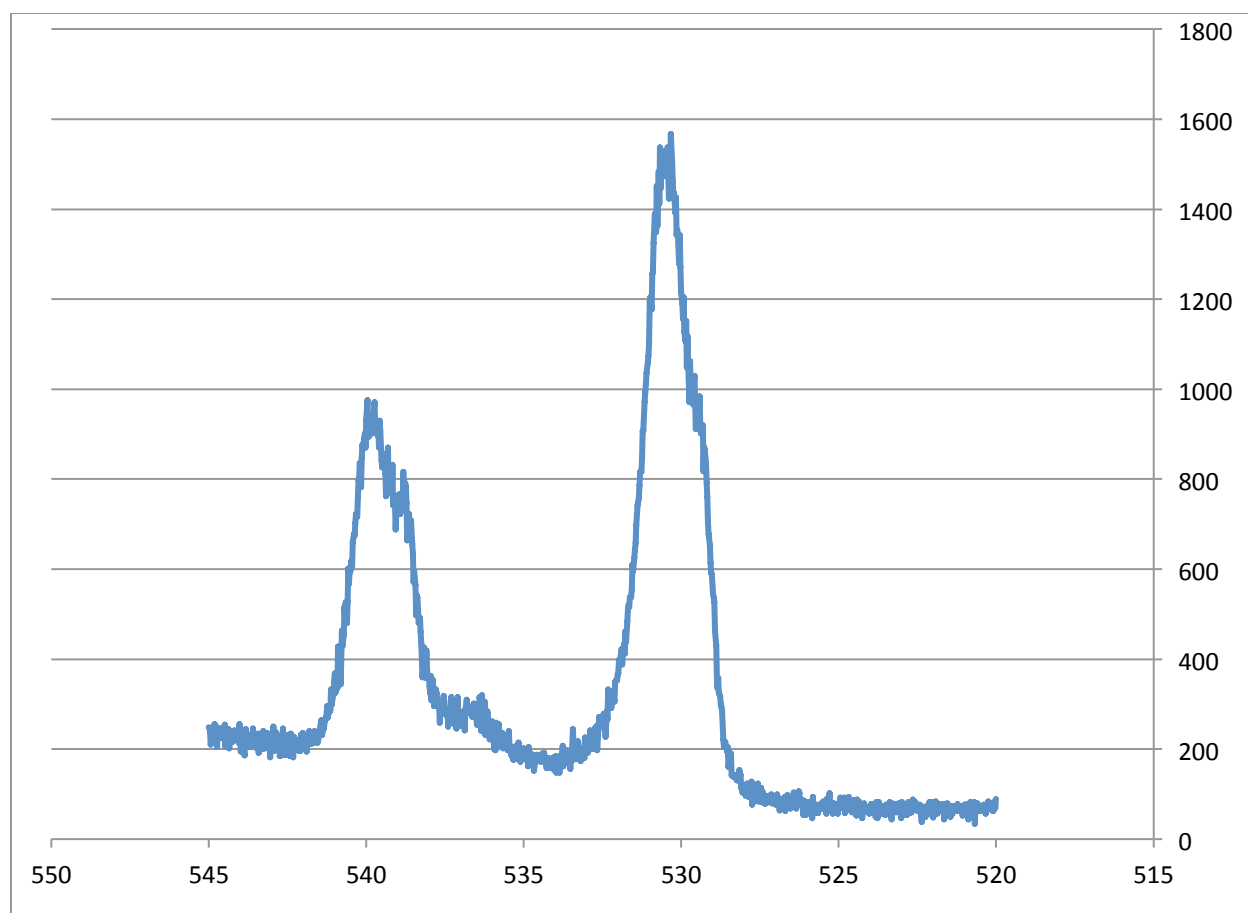


Figure 11: XPS Spectrum of the Sb 3d region (545 - 520 eV) at a Pass Energy of 23.50 eV

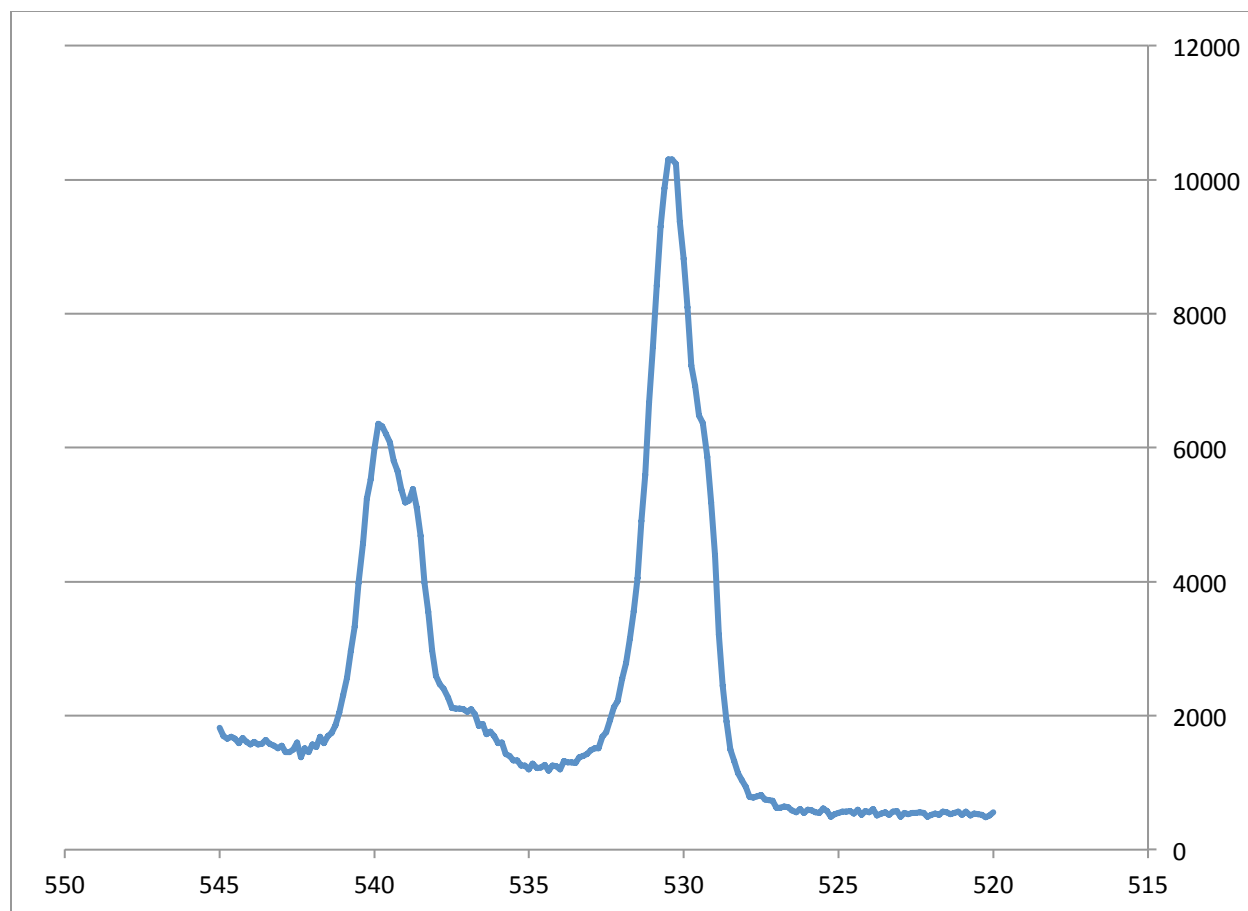


Figure 12: XPS Spectrum of the Sb 3d region (545 - 520 eV) at a Pass Energy of 29.35 eV

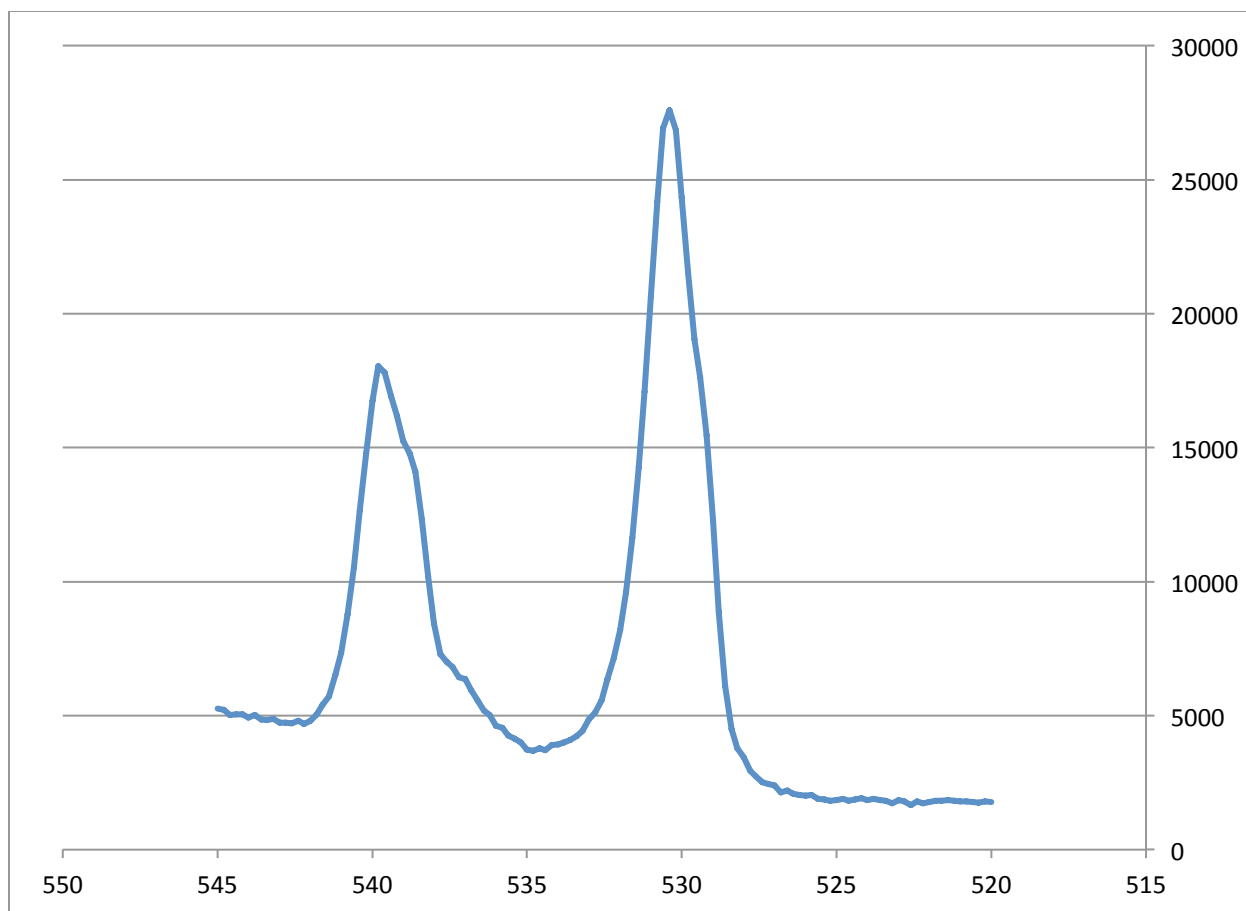


Figure 13: XPS Spectrum of the Sb 3d region (545 - 520 eV) at a Pass Energy of 46.95 eV

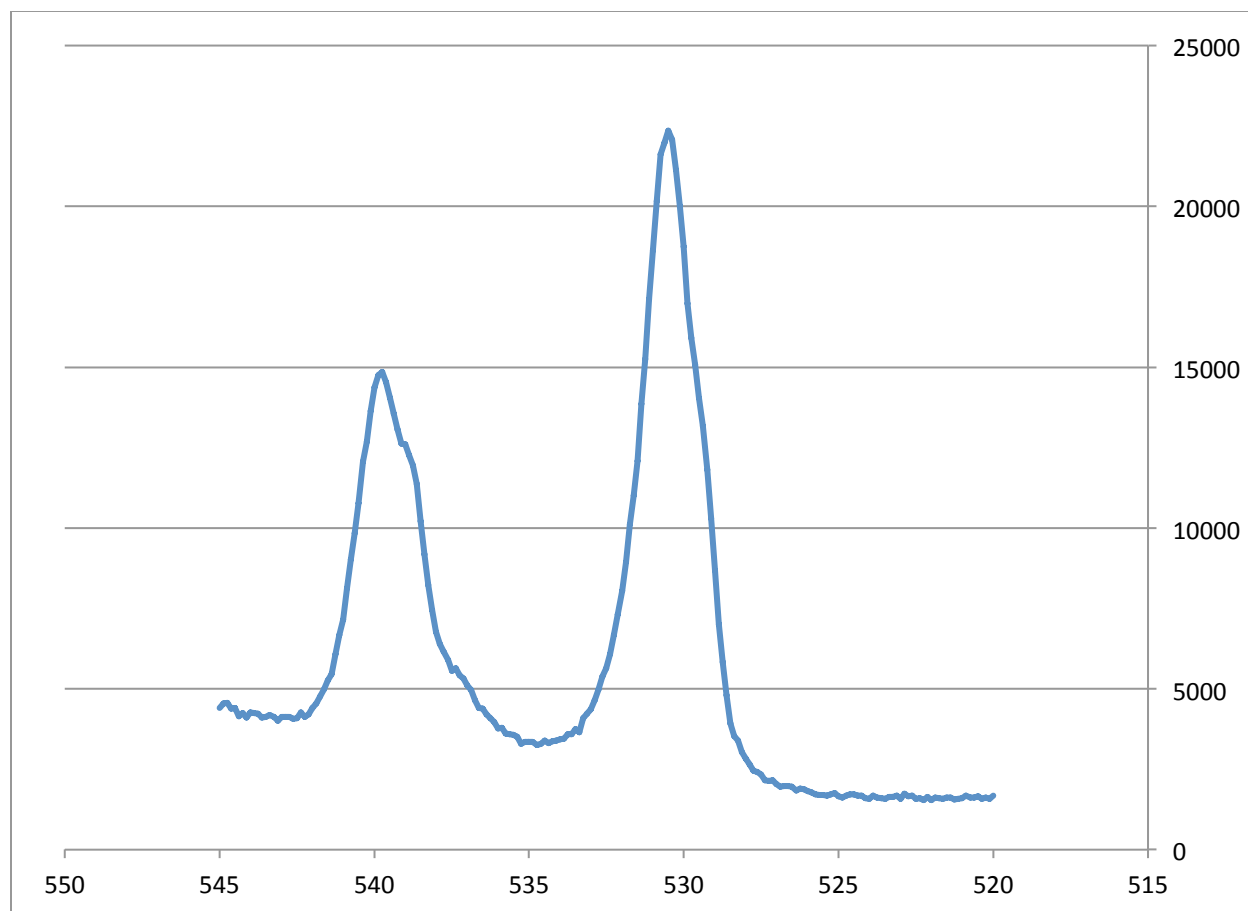


Figure 14: XPS Spectrum of the Sb 3d region (545 - 520 eV) at a Pass Energy of 58.70 eV

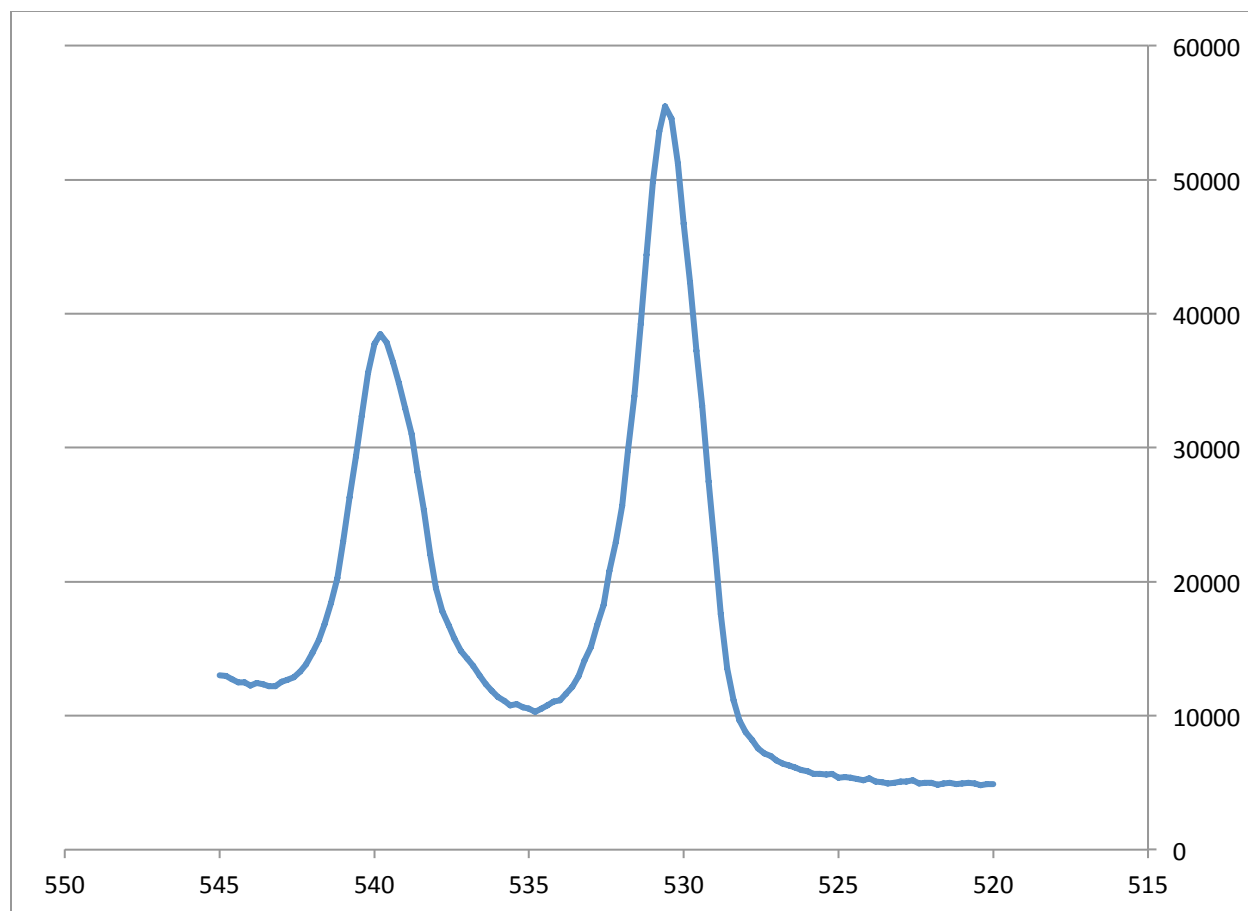


Figure 15: XPS Spectrum of the Sb 3d region (545 - 520 eV) at a Pass Energy of 93.90 eV

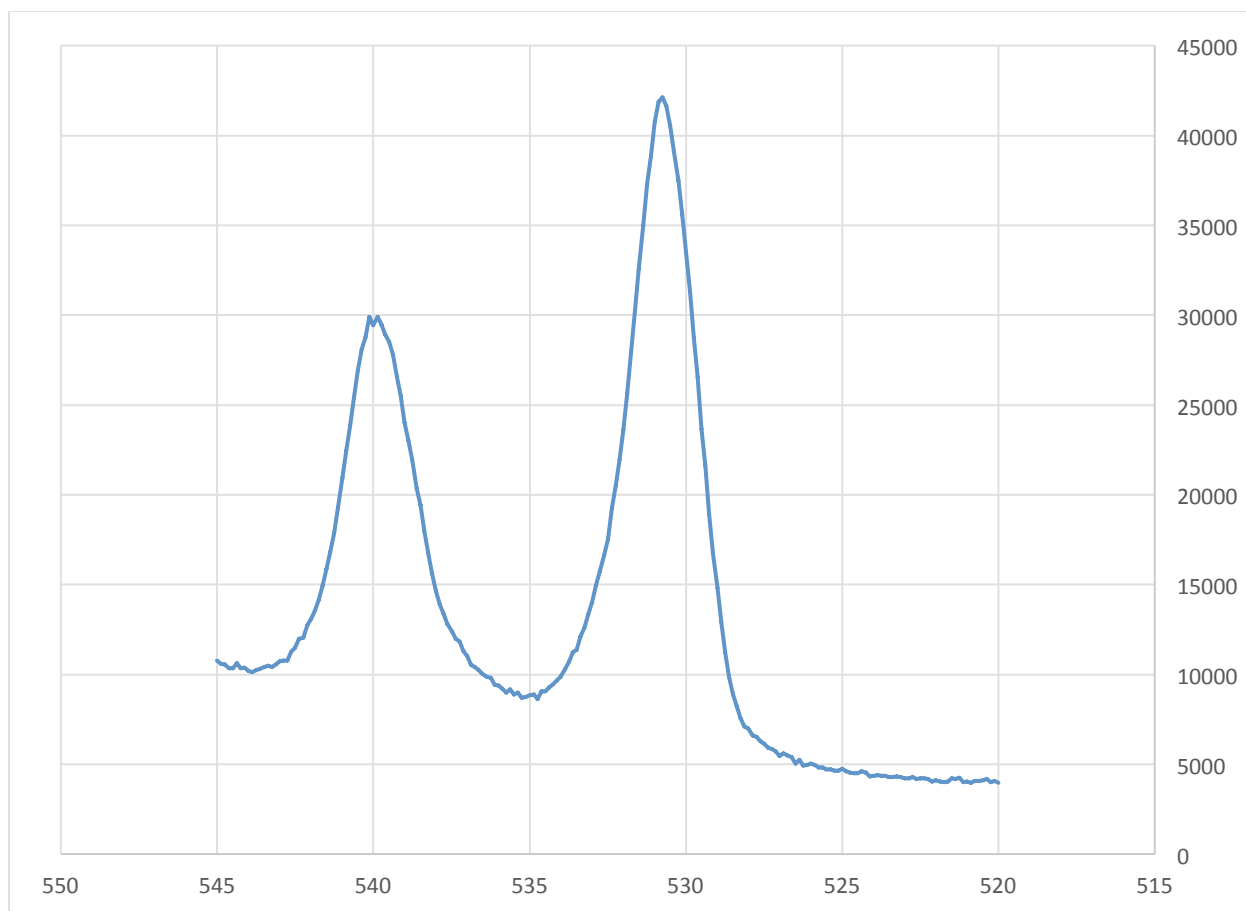


Figure 16: XPS Spectrum of the Sb 3d region (545 - 520 eV) at a Pass Energy of 117.40 eV

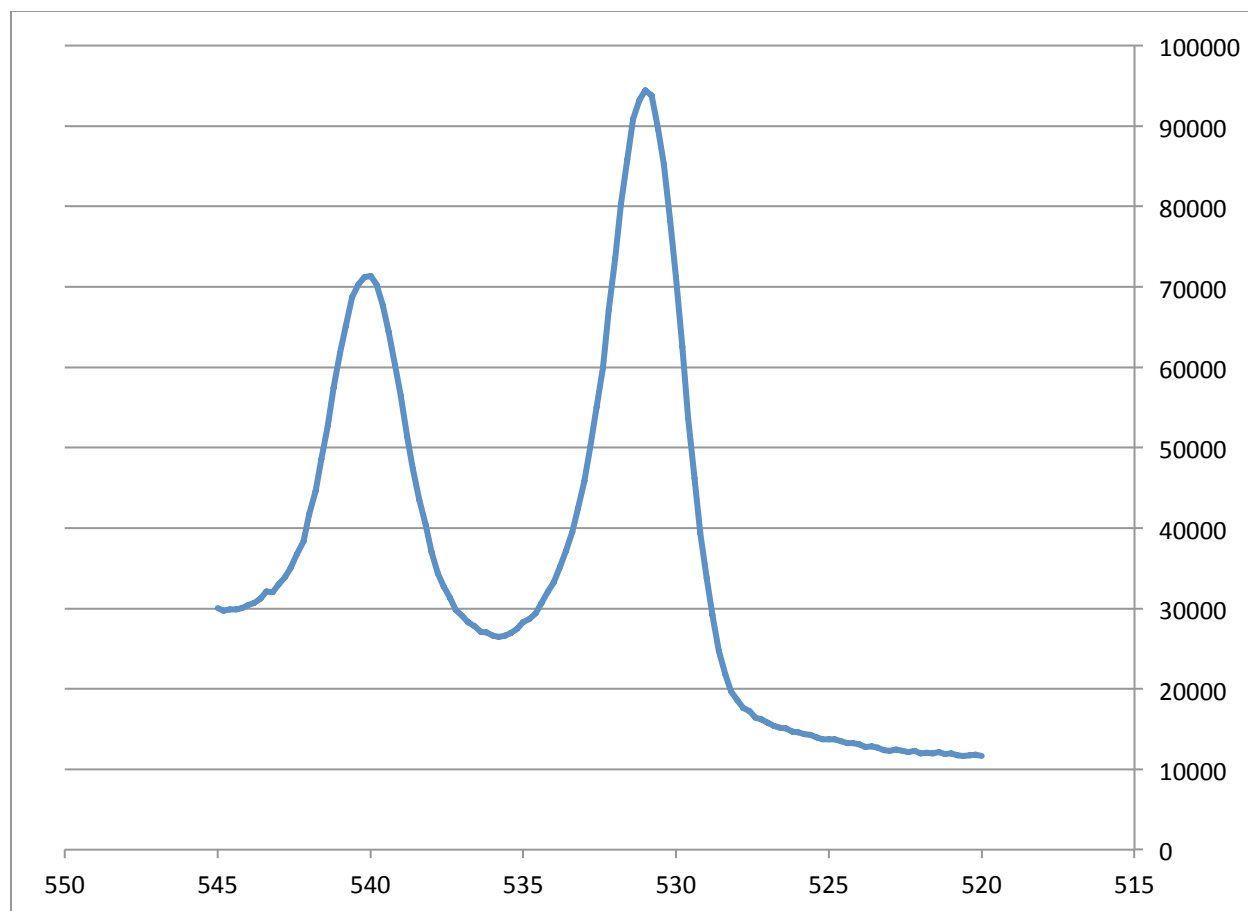


Figure 17: XPS Spectrum of the Sb 3d region (545 - 520 eV) at a Pass Energy of 187.85 eV